Flow Coulometry with Ring-Disk Electrode

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A flow coulometric method using a ring-disk electrode is proposed, in which the coulometric titration is performed at the disk electrode under the control of the ring electrode memorizing the reference potential so as to indicate an end point. Some preliminary studies are presented using for an example the typical coulometric titration reaction between electrogenerated bromine and arsenious ion. Arsenious ion can be determined over the concentration range from 10^{-5} *M* to 10^{-3} *M*.

KEY WORDS: Flow coulometry/ Ring-disk electrode/ Coulometric titration/ Arsenious ion/ Electrogenerated bromine/

INTRODUCTION

The rotating ring-disk electrode has recently become of interest as a useful technique not only for the elucidation of electrode mechanisms but also for the study of homogeneous reactions. Whereas a few analytical applications of the ring-disk electrode have been reported. Johnson and Allen[1] have reported a successful application of the ring-disk electrode to the stripping voltammetry with collection for the determination of down to 1.0×10^{-10} *M* Ag^+ in 0.1 *M* sulfuric acid. Brückenstein and Johnson[2,3] have presented a unique technique; a coulometric diffusion layer titration with amperometric end point detection, in which the theoretical treatment of the titration curve was presented.

The authors have planed to develop a flow coulometry using a ring-disk electrode, and present here its principle and some preliminary studies using for an example the typical coulometric titration reaction between electrogenerated bromine and arsenious ion. The principle of the method is illustrated in Fig. 1, where the disk electrode is used for the electrogeneration of titrants in pairs with the platinum auxiliary cathode, and the ring electrode is used as a regulator electrode. After setting the ring electrode to the reference potential against the saturated calomel electrode (SCE), which corresponds to the end point potential, the coulometric titration is carried out at the disk electrode and continued until the ring electrode indicates the end point.

As well known, arsenious ion can be oxidized quantitatively with bromine generated by the electrooxidation of bromide in acidic media according to Eqs. (1) and (2).

$$2Br^- \rightleftarrows Br_2+2e \quad (1)$$

$$As(III)+Br_2 \rightleftarrows As(V)+2Br^- \quad (2)$$

If the current efficiency for the electrooxidation of bromide is 100% and the rates

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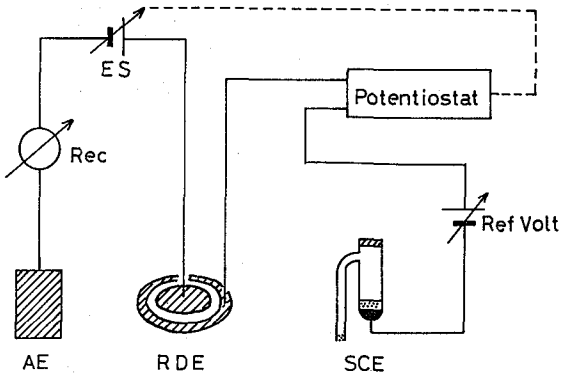

Fig. 1. Principle of flow coulometry with ring-disk electrode
AE: auxiliary Pt electrode, RDE: ring-disk electrode, Ref Volt: end point potential, ES: electrolysis source, and Rec: recorder.

of the electrode and titration reactions are enough fast in comparison with that of mass transfer, the instantaneous disk current is proportional to the concentration of arsenious ion and the surface concentration of bromine at the disk electrode will remain zero until the end point. After the end point, excess bromines produced at the disk will reach to the ring by convective radial flow and diffusion. Some fundamental relationships between the disk current and the ring potential, and the concentration of arsenious ion were discussed.

EXPERIMENTAL

Reagents and Apparatus

All chemicals used were of analytical reagent grade, and deionized water was used after distilled from an all-quartz distillation ware. The supporting electrolyte was composed of 0.2 *M* KBr and 0.1 *M* H_2SO_4.

The ring-disk electrode used here consisted of the glassy carbon disk of 5.0 mm in diameter (GC-20 from Tokai Denkyoku, Nagoya) covered with an insulating thin tube of teflon, and a concentric platinum ring of 5.8 mm in inner-diameter and 7.8 mm in

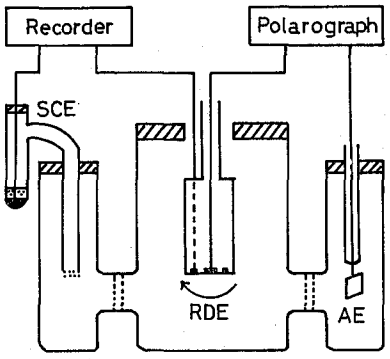

Fig. 2. Electrolysis cell assembly
AE: auxiliary Pt electrode, and RDE: ring-disk electrode.

outer-diameter. Figure 2 shows the schematic diagram of the electrolysis cell, where the ring and disk electrodes can be controlled independently. The anodic disk current was scanned linearly with time between the disk anode and the platinum auxiliary cathode using a Yanagimoto Polarograph Model P8. The electrode potential of the ring indicator electrode was recorded against SCE as a function of time, using a National Pen Recorder Model VP653B.

RESULTS

Current Efficiency. The current efficiency of the electrooxidation of bromide at the disk electrode was measured by means of the constant current coulometric titration with the standard solution of arsenious ion, and was estimated as 98.4% with the relative standard deviation of 0.3%.

Potential—Time Profile at the Ring Electrode. Figure 3 shows the potential variation of the ring electrode during the coulometric titration, in which the disk current was scanned at the rate of 1.67×10^{-6} A/sec, and the electrode was rotated at the speed of 800 rpm. In the figure, as an instantaneous disk current is proportional to the titration time, the electrode potential of the ring (E_R) is plotted against the disk current (i_D). As a result, 650 mV *vs.* SCE was taken as the end point potential in this

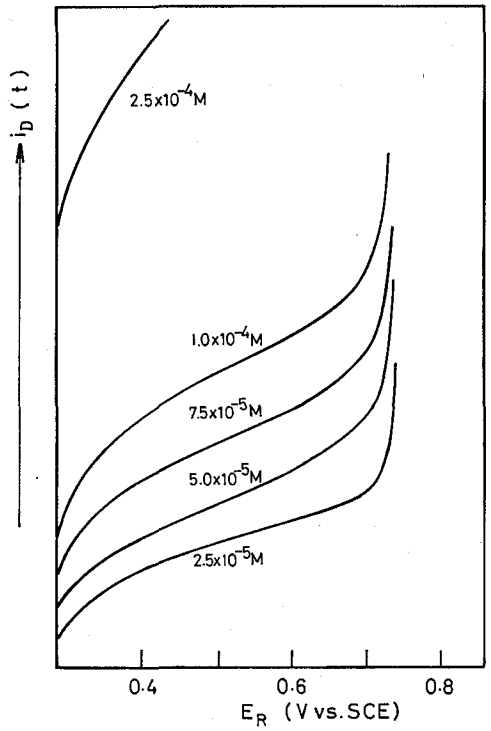

Fig. 3. Potential–time curves at ring electrode
Electrolysis solution: 0.2 *M* KBr in 0.1 *M* H_2SO_4, current scanning rate: 1.67×10^{-6} A/sec, and electrode rotation speed: 800 rpm.

titration. In case of high concentration of As(III), however, the rate of current scan should be faster to get the good result.

Calibration Curve. Figure 4 shows a linear relationship between the concentration of As(III) and the titration time, which was replaced by the disk current at the end point (I_D). In the figure, the background current obtained in the blank experiments was compensated, which seemed to be correspond to the transition time of bromine

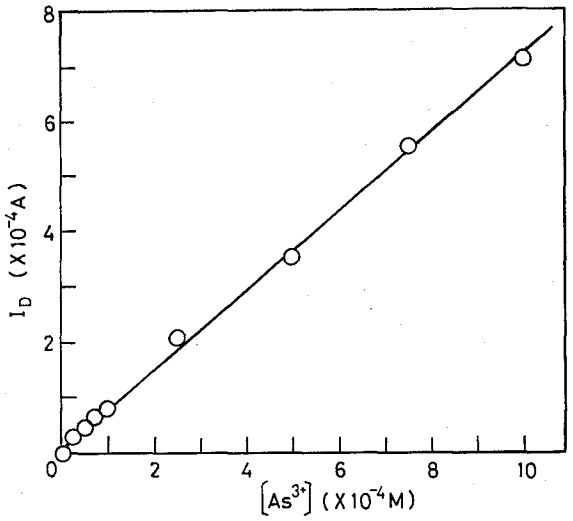

Fig. 4. Calibration curve for As^{3+}
End point potential: 650 mV *vs.* SCE, and other conditions are the same as those in Fig. 3.

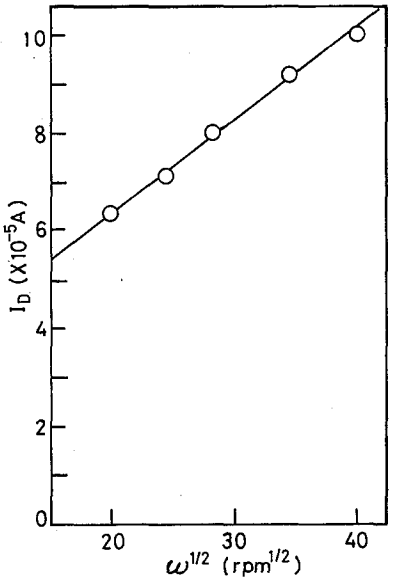

Fig. 5. Dependence of I_D on electrode rotation speed
$[As^{3+}]$: 10^{-4} *M*, and other conditions are the same as those in Fig. 4.

from the disk to ring.

Effect of Rotation Speed of the Electrode. Figure 5 shows a linear relationship between the disk current at the end point (I_D) and the square root of the electrode rotation speed ($\omega^{1/2}$) in the titration of 1.0×10^{-4} *M* As(III).

It is ascribed that arsenious ion can be determined by this method over the concentration range from 10^{-5} *M* to 10^{-3} *M*.

The development of a new potentiostat, in which the coulometric titration at the disk electrode can be controlled automatically by the detection of the ring potential, will enable the method more applicable for the monitoring of concentration in the flowing system. This automatic titrator system using a ring-disk electrode will be developed and presented elsewhere.

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